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Author Response for "Revisiting the reaction of dicarbonyls in aerosol proxy solutions containing ammonia: the case of butenedial" by Jack C. Hensley et al.

We thank the anonymous referee for their thoughtful comments, which have helped improve the manuscript. Our replies are below (referee comment in bold face, response in normal face, manuscript indented with new content in italics, maintained content in normal face, and removed content in strike-through).

General comments:
This manuscript describes results from an analysis of the reactions that can occur for butenedial in aqueous solution as a function of pH and as a function of NHx concentration. The chemical changes were tracked with NMR combined with some MS to help identify products and a chemical scheme along with reaction kinetics are provided. Overall, this work demonstrates the need for additional studies on different types of dicarbonyls that are atmospherically relevant as the behavior of butenedial does not follow what would be predicted based on prior studies of a-dicarbonyls like glyoxal and methylglyoxal. This is a well written and clear study that builds on prior work. I would recommend acceptance in ACP after the following minor comments are addressed:

Minor comments:

1. **The accretion products from betenedial/OH- were observed to be brown immediately, and a portion of the MS is provided for the samples (figure S4). Were there any nitrogen containing peaks observed to form in this sample in the other mass ranges? I am concerned about trace ammonia from the room since very small concentrations would be needed if the chromophores have a large absorption cross section.**

Thank you for this comment. To confirm that butenedial/OH^- products are light-absorbing, new measurements with high resolution LC-MS-UV/Vis were taken of butenedial/OH^- reaction mixtures. As shown in Figure S5, reprinted below, we observe evidence for proposed hydroxy acid oligomer products, with unambiguous molecular formula $C_{4n}H_{4n+1}O_{2n+1}^-$ (deprotonated under pH conditions of mixture). As shown in Figure S6, reprinted below, these products absorb in the 300-450 nm wavelength range. Additionally, we did not observe evidence of butenedial/NH_X reaction products in butenedial/OH^- reaction mixtures with LC-MS operated in positive mode.

Figure S5.

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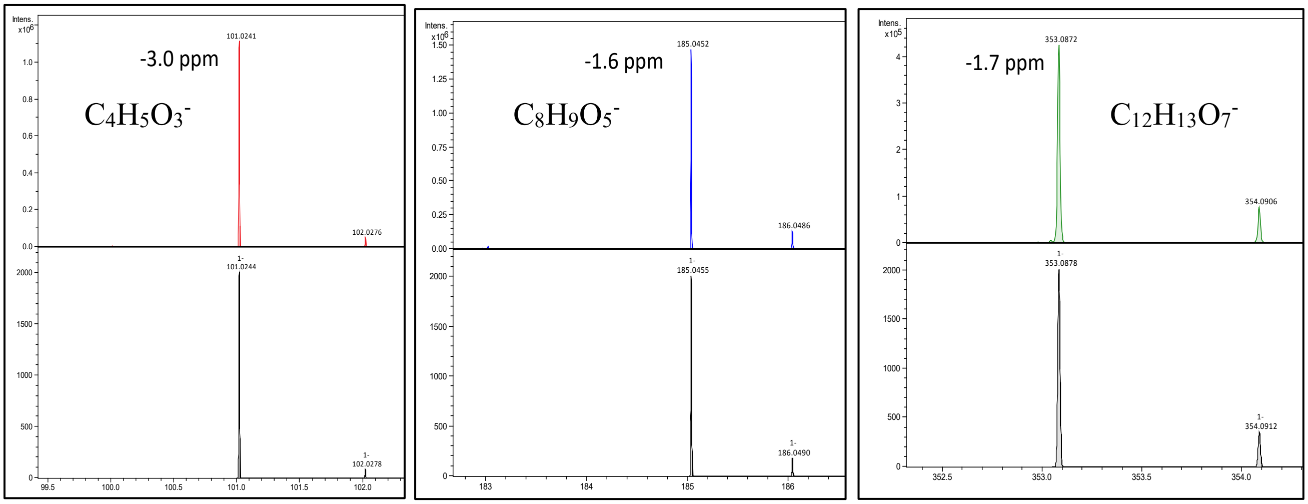
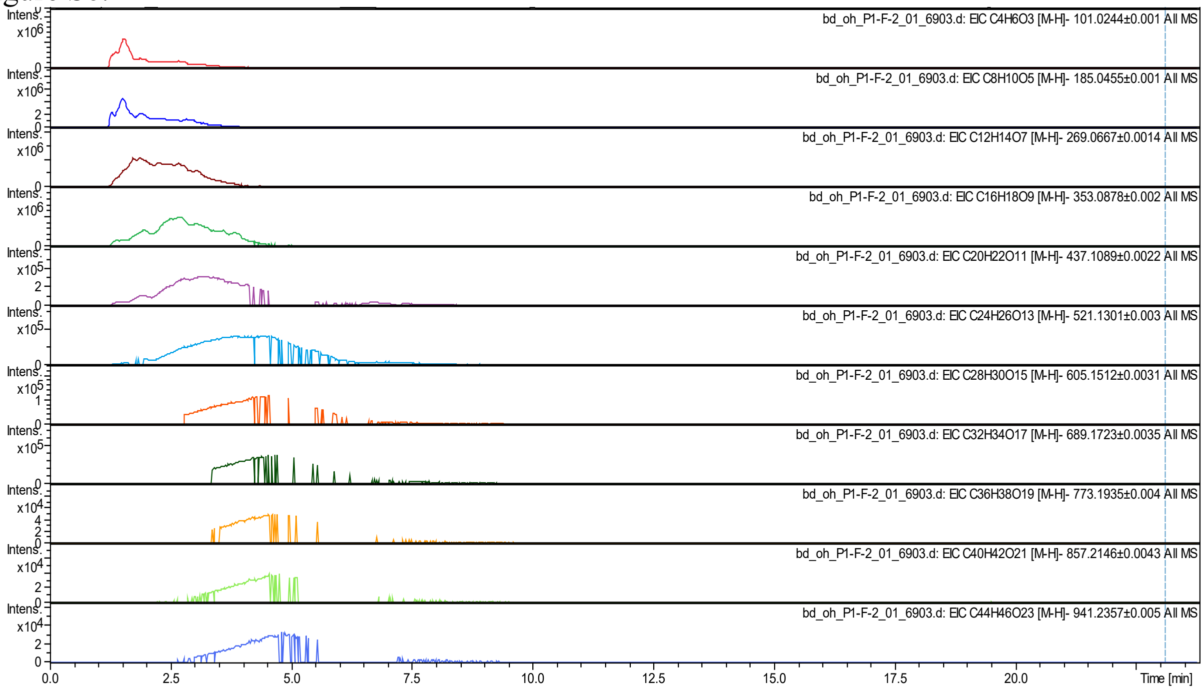


Figure S6.



2. **The concentration ranges here were reasonably high, what do these concentration ranges correspond to in the atmosphere? There is some discussion about rainwater in India, given the much lower concentrations for organics that can be found in rainwater, would the authors expect to see the same types of chemistry?**

Butenedial concentrations are unknown in the atmosphere, as to the best of our knowledge, butenedial has not yet been quantitatively measured. The measurements by Matsunaga et al. (2004) for 4-oxopentanal, a saturated 1,4-ketoaldehyde, suggest that larger dicarbonyls could be as abundant as 1,2-dicarbonyls, with concentrations in aerosol ranging from 6-60 mM. Such concentrations are 1-2 orders of magnitude less than those we used in this study. Unlike for glyoxal, we do not find evidence for a dependence on butenedial concentration in the reaction rate law. As Reviewer 1 pointed out, others have suggested that glyoxal may switch to a first order dependence at low concentrations, as under these conditions, the bimolecular reaction of glyoxal and NH_X may be the rate limiting step (Nozière et al., 2009; Sedehi et al., 2013). Pyrrolinone formation is shown to be first order with respect to butenedial regardless of whether imine formation or ring-closure is the rate limiting step.

Research on the pH of rainwater in India is alkaline due to dissolution of Ca^{2+}-rich aerosols (Kulshrestha et al., 2001). We therefore take this as a proxy for geographical location in which pH conditions could be basic enough to favor butenedial/NH_X reaction. The manuscript is updated to make this point more clearly. It also includes the North China Plain as another similar region with high NH_X and pH, lines 371-374:

> It is, however, likely that condensed phase reaction of butenedial with NH_X could regionally be important, specifically at close to neutral pH and high NH_X, such as in agricultural areas in India *or the North China Plain* where NH_3 emissions are high (Kuttippurath et al., 2020*; Zhang et al., 2010*) and ~~rainwater is observed to be alkaline~~ *aerosol may be alkaline* (Kulshrestha et al., 2001; *Tao et al., 2020*).

3. **On page 7, it is stated that the 1H-NMR spectra shows a buildup of signal in the baseline which increases and spreads out with respect to the chemical shift over time. With the data overlaid and colored the way it is, this is very difficult to see in the figure. Also in Figure S5, there is a note that there are two expanded regions, but these are not shown in the figure.**

Figure S7 (previously Figure S5), reproduced below, contains the described expanded regions to improve visibility of the buildup of signal in the baseline, and is reprinted below. Additionally, we provide new evidence of the accretion reactions that cause the observed build-up in the baseline through high-precision LC-MS measurements of hydroxycrotonic acid oligomers in butenedial/OH^- reaction mixtures (see Figure S5 above).

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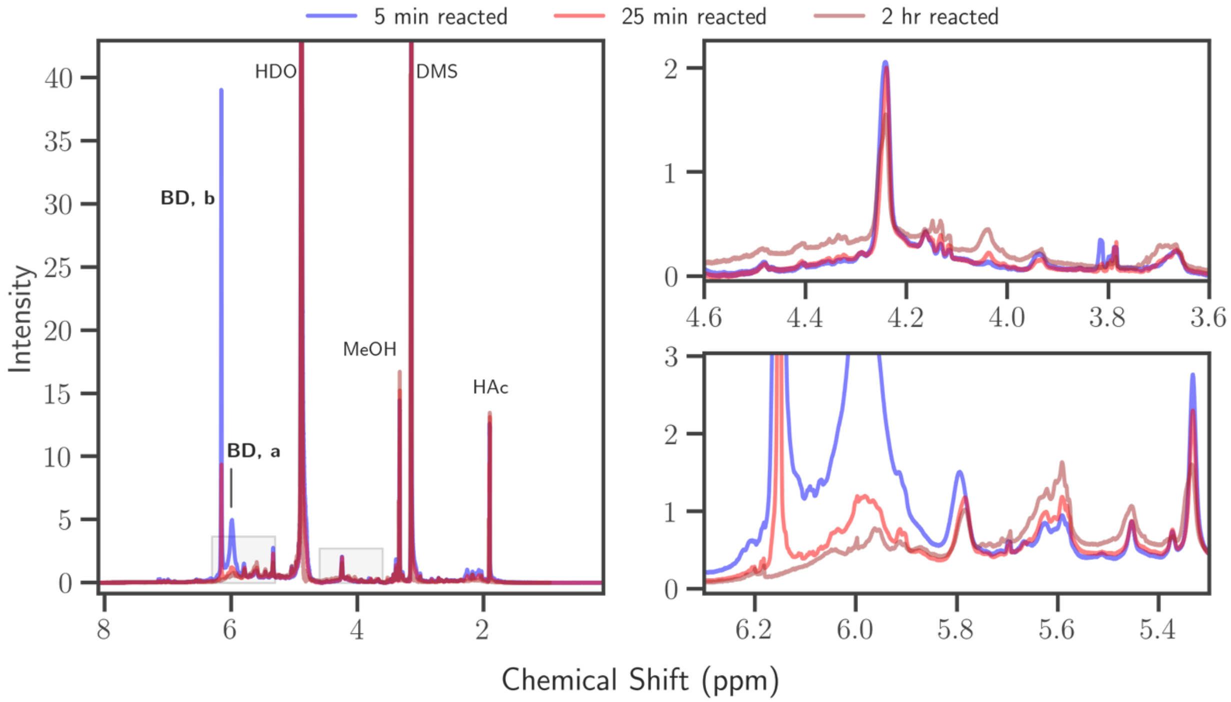
Figure S7.



4. **The numerical values for the last few supplemental figures appear to be off in the manuscript (there is no Figure S16).**

References to the supplemental section now have been checked to ensure that they match the correct figures.

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